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The crystal chemistry of lithium in the alluaudite structure: a study of the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ solid solution ($x = 0$ to 1)

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Summary

Phosphates of compositions $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ were synthesized by solid state reactions in air, and pure alluaudite-type compounds were obtained for $x = 0.00$, 0.25, and 0.50. Rietveld refinements of X-ray powder diffraction data indicate the occurrence of Mn^{2+} in the $M(1)$ site, and of Fe^{3+} and Mn^{2+} in the $M(2)$ site. For $x = 0.25$ and 0.50, $A(1)$ is occupied by Li^+ and Na^+, whereas $A(2)$' is occupied by Na^+ and vacancies. A careful examination of the number of electrons occurring in the A sites of the alluaudite-type compounds $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ confirms that lithium occupies only the $A(1)$ crystallographic site of the alluaudite structure.

Introduction

The alluaudite mineral group comprises Na-Mn-Fe-bearing phosphates which are known to occur in granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the recent classification of *Černý* (1991). The crystal structure of natural alluaudite has been determined by *Moore* (1971) in the monoclinic $C2/c$ space group, and he proposed the general structural formula, $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with $Z = 4$.

More recently, several structure refinements of synthetic phosphates with the alluaudite structure were performed (*Yakubovich* et al., 1977; *Antenucci*, 1992; *Antenucci* et al., 1993, 1995; *Warner* et al., 1993; *Lii* and *Shih*, 1994; *Leroux* et al., 1995a, b; *Lii* and *Ye*, 1997; *Korzenski* et al., 1998; *Hatert* et al., 2000, 2002, 2003, 2004; *Chouaibi* et al., 2001; *Guesmi* and *Driss*, 2002; *Daidouh* et al., 2002;

Ben Smail and *Jouini*, 2002; *Durio* et al., 2002; *Hidouri* et al., 2003), which clearly demonstrate the existence of three cationic sites that were not reported by *Moore* (1971). These sites are located in channels on crystallographic positions which are different from those of $X(1)$ and $X(2)$. Based on detailed structural studies, *Hatert* et al. (2000) proposed a new general formula, $[A(2)A(2)'][A(1)A(1)'A(1)''_2]M(1)M(2)_2[PO_4]_3$, for alluaudite-type compounds.

In granitic pegmatites, alluaudite displays chemical compositions ranging from $Na_2Mn(Fe^{2+}Fe^{3+})(PO_4)_3$ to $\square NaMnFe^{3+}{}_2(PO_4)_3$, with Mn^{2+} or some Ca^{2+} replacing Na^+ on the $A(1)$ site, Fe^{2+} replacing Mn^{2+} on the $M(1)$ site, and Mg^{2+} or Mn^{2+} replacing iron on the $M(2)$ site, where $\square$ represents a lattice vacancy on the $A(2)'$ site. *Moore* (1971) considered that Li^+ was localized on the $M(2)$ site of the structure, because the ionic radius of this cation is particularly small (*Shannon*, 1976). However, no structural or spectroscopic data were presented by *Moore* (1971) to confirm this contention.

The geochemical role of lithium is essential in rare-element alluaudite-bearing granitic pegmatites. Li-bearing alluaudites are of interest as candidates for lithium battery cathodes (*Richardson*, 2003). We thus decided to investigate the crystal-lochemical role of lithium in the alluaudite structure. With this goal in mind, *Hatert* et al. (2000) synthesized the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ solid solution and performed single-crystal X-ray structure refinements on these compounds, whereas *Hatert* et al. (2002) synthesized the $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ series on which X-ray Rietveld refinements and infrared spectroscopic measurements were performed. The wet chemical analyses of $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ (*Hatert* et al., 2000) have clearly demonstrated that lithium is incorporated in the alluaudite structure, and the crystal structure refinements of $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ (*Hatert* et al., 2000, 2002) have shown that this cation was not localized on the octahedral M sites of the structure, but on the large A sites. However, the distribution of Na^+ and Li^+ on the $A(1)$ and $A(2)'$ crystallographic sites was not accurately determined, because the electronic densities involved in the $Na^+ \rightarrow Li^+$ substitution are small.

In order to shed more light on the distribution of Na^+ and Li^+ between the $A(1)$ and $A(2)'$ crystallographic sites, the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ alluaudite-type solid solution was synthesized by solid state methods. Rietveld refinements of X-ray powder diffraction data were carried out to investigate the structural consequences of the $Na^+ \rightarrow Li^+$ replacement more accurately than in the solid solutions previously investigated by *Hatert* et al. (2000, 2002), because the number of vacancies per formula unit is lower in the alluaudites synthesized in the present study.

Experimental

Compounds of the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ series, with x ranging from 0.00 to 1.00, have been synthesized through a solid state reaction carried out in air. Stoichiometric quantities of $NaHCO_3$ (Merck, >99.5%), Li_2CO_3 (Merck, 99.99%), MnO (Alfa, 99.5%), $FeSO_4 \cdot 7H_2O$ (Merck, >99.5%), and $(NH_4)H_2PO_4$ (Merck, >99%) were dissolved in concentrated nitric acid and the resulting solution was evaporated to dryness. The dry residue was progressively heated in a platinum crucible, at a heating rate of 500°/h, to 900 °C and then maintained at

Table 1. *Unit-cell parameters for synthetic alluaudite-type compounds* $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$

x	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
0.00	12.018(2)	12.591(2)	6.442(1)	114.27(1)	888.6(2)
0.25	12.013(2)	12.543(2)	6.427(1)	114.57(1)	880.7(2)
0.50	12.006(2)	12.515(2)	6.426(1)	114.78(1)	876.6(2)
0.75*	12.002(2)	12.510(2)	6.428(2)	114.96(1)	875.0(2)
1.00*	11.982(3)	12.514(2)	6.409(2)	115.12(2)	870.1(2)

* Alluaudite + $Li_3Fe_2(PO_4)_3$

this temperature for 17 to 65 hours. Alluaudite-type compounds were obtained by quenching the product in air.

X-ray powder diffraction patterns of the compounds were recorded with a Philips PW-3710 diffractometer using Fe$K\alpha$ radiation ($\lambda = 1.9373$ Å). The unit-cell parameters (Table 1) were calculated with the least-squares refinement program LCLSQ 8.4 (*Burnham*, 1991) from the d-spacings calibrated with $Pb(NO_3)_2$ as an internal standard. These unit-cell parameters, and the atomic positions reported for $NaMnFe_2(PO_4)_3$ (*Hatert* et al., 2000), served as starting parameters for the Rietveld refinements which were performed with the DBWS-9807 program (*Young* et al., 1998). The 2θ-range investigated extended from 10 to 100°, the step width was 0.02°, and the step time was 15 s. The total number of refined parameters was 55 ($x = 0.00$), 56 ($x = 0.25$) or 54 ($x = 0.50$), with 504 ($x = 0.00$), 490 ($x = 0.25$) or 498 ($x = 0.50$) observed reflections. The final Rietveld plot for $Na_{0.75}Li_{0.75}Mn_{1.5}Fe_{1.5}(PO_4)_3$ is shown in Fig. 1, and fits of

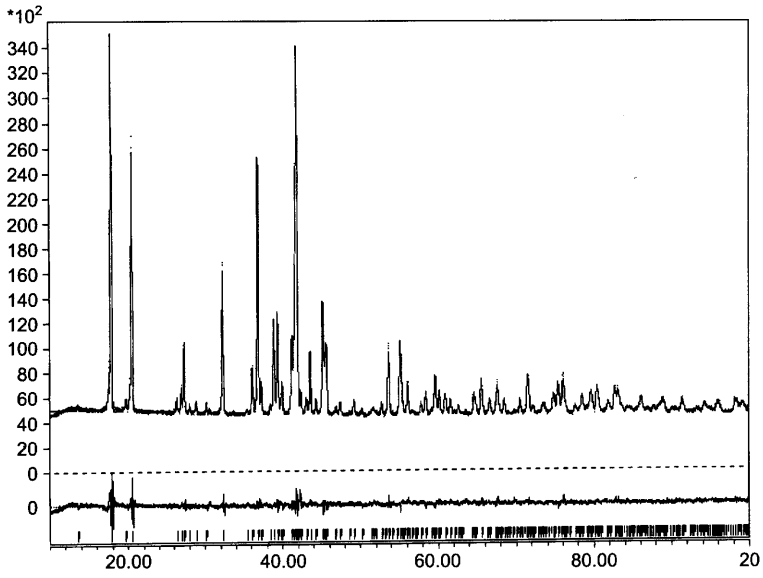

Fig. 1. The observed (dots), calculated (solid line), and difference X-ray powder diffraction patterns of $Na_{0.75}Li_{0.75}Mn_{1.5}Fe_{1.5}(PO_4)_3$ obtained from a Rietveld refinement. The vertical markers indicate the positions calculated for the Fe-$K\alpha_1$ and Fe-$K\alpha_2$ Bragg reflections

equivalent quality were obtained for $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ and $Na_{1.125}Li_{0.375}Mn_{1.5}Fe_{1.5}(PO_4)_3$.

Crystal chemistry of $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$

X-ray powder diffraction patterns of the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ solid solution indicate that pure alluaudite-like compounds are obtained for x values between 0.00 and 0.50, whereas the alluaudite-type phases are associated with $Li_3Fe_2(PO_4)_3$ (*Winand* et al., 1990) for $x = 0.75$ and 1.00. Consequently, the maximum Li-content of the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ solid solution is located between $x = 0.50$ and $x = 0.75$, and the value $x = 0.70$ is chosen as a reasonable substitution limit because the observed amount of $Li_3Fe_2(PO_4)_3$ is very small for $x = 0.75$. It is also interesting to note that $Li_3Fe_2(PO_4)_3$ has already been observed in association with alluaudite by *Hatert* et al. (2000) in the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ solid solution for $x = 0.95$ and 1.00.

The reliability factors, positional parameters, site occupancies, and interatomic distances and angles, deduced from the Rietveld refinements, are given in Tables 2, 3, and 4, respectively. Both the satisfactory values of R_p, R_{wp}, R_{Bragg}, and S (Table 2), and the mean O–P(1)–O and O–P(2)–O angles (Table 4), which are close to those of an ideal tetrahedron, confirm the reliability of the refinements. A polyhedral representation of the crystal structure of $Na_{0.75}Li_{0.75}Mn_{1.5}Fe_{1.5}(PO_4)_3$, projected along the approximate [001] direction, is shown in Fig. 2.

The crystallographic sites of the alluaudite-like compounds (Table 3) are labeled according to the nomenclature recently proposed by *Hatert* et al. (2000). The morphologies of the coordination polyhedra of $M(1)$ and $M(2)$ are those of distorted octahedra, whereas the morphologies of $A(1)$ and $A(2)'$ are those of a distorted cube and of a gabled disphenoid, respectively. These morphologies are similar to those previously described for the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ compounds (*Hatert* et al., 2000).

The localization of iron and manganese is not easy to establish, because these cations cannot be distinguished by Rietveld refinements of X-ray data. Moreover, the Mössbauer spectral investigation of the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ alluaudite-type solid solution by *Hermann* et al. (2002) has shown the unexpected presence of up to 19% Fe^{2+} on the $M(2)$ site of the structure. In order to check the presence of Fe^{2+} in the compounds under study, we measured the Mössbauer spectrum of $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ at 295 K, using experimental conditions similar to those

Table 2. *Reliability factors for the Rietveld refinements of the alluaudite-type compounds* $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$

x	0.00	0.25	0.50
R_p (%)	1.74	1.80	2.06
R_{wp} (%)	2.35	2.47	2.93
$R_{exp.}$ (%)	1.37	1.38	1.35
S	1.71	1.78	2.15
R_{Bragg} (%)	3.40	4.05	4.89

Table 3. *Positional (x, y, z), isotropic thermal (B) and site occupancy (N) parameters for the synthetic alluaudite-type compounds* $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$

Site	Atom	Wyckoff	*x*	*y*	*z*	*B* (Å^2)	*N*
$x=0.00$							
A(2)′	Na	4*e*	0	−0.0097(9)	1/4	0.1(5)	0.247(4)
A(1)	Na	4*b*	1/2	0	0	1.8(2)	0.516(4)
M(1)	Mn	4*e*	0	0.2665(3)	1/4	0.4(2)	0.487(4)
M(2)	Mn	8*f*	0.2803(2)	0.6553(2)	0.3654(4)	0.76(9)	0.246(8)
	Fe	8*f*	0.2803(2)	0.6553(2)	0.3654(4)	0.76(9)	0.75
P(1)	P	4*e*	0	−0.2823(4)	1/4	0.4(1)	1.0
P(2)	P	8*f*	0.2383(3)	−0.1065(3)	0.1298(6)	0.4(1)	1.0
O(1)	O	8*f*	0.4578(5)	0.7115(5)	0.535(1)	0.6(1)	1.0
O(2)	O	8*f*	0.1004(6)	0.6375(4)	0.2405(9)	0.6(1)	1.0
O(3)	O	8*f*	0.3286(5)	0.6635(5)	0.104(1)	0.6(1)	1.0
O(4)	O	8*f*	0.1257(5)	0.4004(4)	0.3222(8)	0.6(1)	1.0
O(5)	O	8*f*	0.2286(5)	0.8234(4)	0.324(1)	0.6(1)	1.0
O(6)	O	8*f*	0.3188(4)	0.5015(6)	0.3810(7)	0.6(1)	1.0
$x=0.25$							
A(2)′	Na	4*e*	0	−0.0077(9)	0.25	1.8(5)	0.281(4)
A(1)	Na	4*b*	0.50	0	0	2.3(3)	0.346(4)
	Li	4*b*	0.50	0	0	2.3(3)	0.1875
M(1)	Mn	4*e*	0	0.2689(3)	0.25	0.9(2)	0.485(4)
M(2)	Mn	8*f*	0.2798(2)	0.6555(2)	0.3625(4)	0.52(9)	0.254(8)
	Fe	8*f*	0.2798(2)	0.6555(2)	0.3625(4)	0.52(9)	0.75
P(1)	P	4*e*	0	−0.2848(4)	0.25	0.3(1)	0.50
P(2)	P	8*f*	0.2385(3)	−0.1065(3)	0.1340(6)	0.3(1)	1.00
O(1)	O	8*f*	0.4567(5)	0.7131(5)	0.537(1)	0.4(1)	1.00
O(2)	O	8*f*	0.0973(5)	0.6378(4)	0.2307(9)	0.4(1)	1.00
O(3)	O	8*f*	0.3256(5)	0.6610(5)	0.098(1)	0.4(1)	1.00
O(4)	O	8*f*	0.1261(5)	0.4044(4)	0.3223(8)	0.4(1)	1.00
O(5)	O	8*f*	0.2302(5)	0.8238(5)	0.328(1)	0.4(1)	1.00
O(6)	O	8*f*	0.3179(4)	0.5013(6)	0.3778(8)	0.4(1)	1.00
$x=0.50$							
A(2)′	Na	4*e*	0	−0.007(1)	0.25	1.0	0.261(3)
A(1)	Na	4*b*	0.50	0	0	1.0	0.135(3)
	Li	4*b*	0.50	0	0	1.0	0.375
M(1)	Mn	4*e*	0	0.2694(3)	0.25	1.0(2)	0.470(4)
M(2)	Mn	8*f*	0.2783(3)	0.6558(2)	0.3602(5)	0.7(1)	0.255(9)
	Fe	8*f*	0.2783(3)	0.6558(2)	0.3602(5)	0.7(1)	0.75
P(1)	P	4*e*	0	−0.2856(4)	0.25	0.3(1)	0.50
P(2)	P	8*f*	0.2387(4)	−0.1065(3)	0.1355(8)	0.3(1)	1.00
O(1)	O	8*f*	0.4552(6)	0.7144(5)	0.533(1)	0.6(1)	1.00
O(2)	O	8*f*	0.0960(7)	0.6350(5)	0.233(1)	0.6(1)	1.00
O(3)	O	8*f*	0.3234(6)	0.6620(6)	0.098(1)	0.6(1)	1.00
O(4)	O	8*f*	0.1253(7)	0.4031(5)	0.318(1)	0.6(1)	1.00
O(5)	O	8*f*	0.2288(6)	0.8232(6)	0.325(1)	0.6(1)	1.00
O(6)	O	8*f*	0.3185(5)	0.5014(7)	0.3776(9)	0.6(1)	1.00

Table 4. *Selected interatomic distances (Å) and angles (°) for the synthetic alluaudite-type compounds* $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$

x	0.00	0.25	0.50	Difference
$A(2)'$–O(6) × 2	2.480(4)	2.482(4)	2.472(5)	−0.01
$A(2)'$–O(6) × 2	2.643(3)	2.640(3)	2.632(4)	−0.01
$A(2)'$–O(1) × 2	2.84(1)	2.86(1)	2.89(1)	+0.05
$A(2)'$–O(3) × 2	2.88(1)	2.85(1)	2.86(1)	−0.02
Mean	2.71	2.71	2.71	0.00
$A(1)$–O(2) × 2	2.306(5)	2.261(5)	2.231(6)	−0.08
$A(1)$–O(4) × 2	2.363(5)	2.327(5)	2.309(5)	−0.05
$A(1)$–O(4) × 2	2.567(4)	2.545(4)	2.564(5)	−0.00
$A(1)$–O(2) × 2	2.984(5)	3.005(5)	2.964(6)	−0.02
Mean	2.56	2.53	2.52	−0.04
$M(1)$–O(1) × 2	2.207(5)	2.227(5)	2.211(6)	+0.00
$M(1)$–O(4) × 2	2.182(6)	2.194(6)	2.169(5)	−0.01
$M(1)$–O(3) × 2	2.284(5)	2.340(5)	2.349(6)	+0.07
Mean	2.22	2.25	2.24	+0.02
$M(2)$–O(6)	1.984(8)	1.981(8)	1.983(9)	−0.00
$M(2)$–O(5)	2.065(6)	2.058(6)	2.077(6)	+0.01
$M(2)$–O(3)	1.997(5)	1.994(5)	1.976(6)	−0.02
$M(2)$–O(2)	1.985(5)	2.007(4)	2.007(6)	+0.02
$M(2)$–O(1)	2.081(5)	2.077(5)	2.075(6)	−0.01
$M(2)$–O(5)	2.191(6)	2.180(7)	2.164(8)	−0.03
Mean	2.05	2.05	2.05	0.00
$M(2)$–$M(1)$	3.331(2)	3.337(2)	3.345(3)	+0.01
P(1)–O(1) × 2	1.547(7)	1.537(7)	1.549(7)	+0.00
P(1)–O(2) × 2	1.594(6)	1.564(5)	1.560(7)	−0.03
Mean	1.57	1.55	1.55	−0.02
O(2)–P(1)–O(2)	101.4(4)	103.2(4)	100.9(4)	
O(1)–P(1)–O(2) × 2	107.8(3)	106.3(3)	106.9(3)	
O(1)–P(1)–O(1)	109.6(4)	108.4(4)	109.8(4)	
O(1)–P(1)–O(2) × 2	115.1(3)	116.5(2)	116.2(3)	
Mean	109.5	109.5	109.5	
P(2)–O(3)	1.560(7)	1.526(7)	1.534(8)	−0.03
P(2)–O(4)	1.536(4)	1.537(4)	1.536(6)	0.00
P(2)–O(5)	1.574(6)	1.560(7)	1.547(8)	−0.03
P(2)–O(6)	1.512(8)	1.500(8)	1.501(9)	−0.01
Mean	1.55	1.53	1.53	−0.02
O(3)–P(2)–O(4)	107.7(3)	106.5(3)	105.5(3)	
O(4)–P(2)–O(6)	112.6(3)	110.5(3)	111.4(3)	
O(3)–P(2)–O(6)	109.0(3)	108.7(3)	109.2(4)	
O(4)–P(2)–O(5)	107.0(3)	108.6(3)	108.5(4)	
O(5)–P(2)–O(6)	111.1(3)	111.6(3)	111.8(4)	
O(3)–P(2)–O(5)	109.4(4)	110.9(4)	110.3(4)	
Mean	109.5	109.5	109.5	

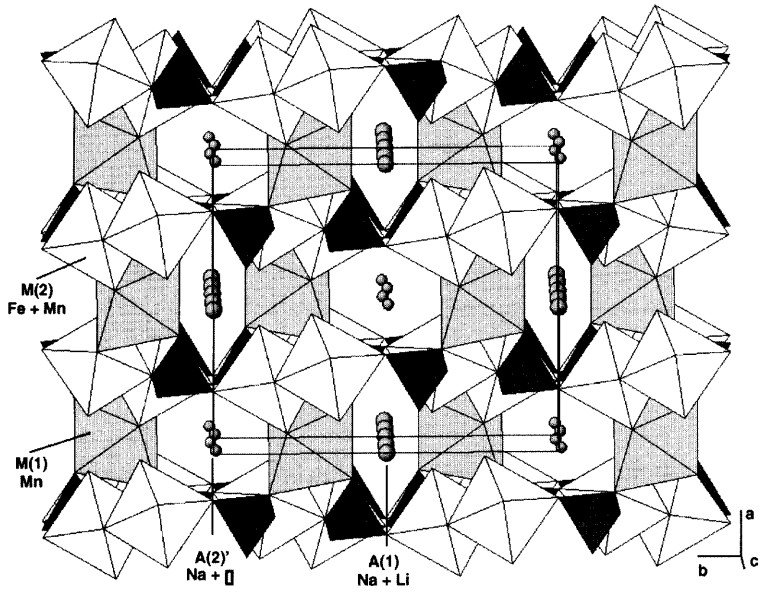

Fig. 2. Projection of the crystal structure of $Na_{0.75}Li_{0.75}Mn_{1.5}Fe_{1.5}(PO_4)_3$. The PO_4 tetrahedra are densely shaded. The shaded $M(1)$ octahedra are occupied by Mn^{2+}, and the unshaded $M(2)$ octahedra are occupied by Fe^{3+} and Mn^{2+}. The spheres represent Na^+ and Li^+ on the $A(1)$ and $A(2)'$ crystallographic sites

described by *Hermann* et al. (2002). The Mössbauer spectral absorber contained 38 mg cm^{-2} of powdered sample. The spectrum exhibits a first doublet with a small isomer shift and quadrupole splitting, assigned to Fe^{3+}, and a second doublet with a large isomer shift and quadrupole splitting, assigned to Fe^{2+}. Qualitatively, the relative area of these doublets indicate the presence of ~5% Fe^{2+}, a value which is significantly smaller than the values observed by *Hermann* et al. (2002) for $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$. Consequently, this small amount of Fe^{2+} was not taken into account in the Rietveld refinements of X-ray powder diffraction data.

Because the ionic radius of Fe^{3+} is significantly smaller than that of Mn^{2+} (*Shannon*, 1976), we decided to consider that Fe^{3+} is localized on the small $M(2)$ site. The Fe-content of this site has thus been fixed to its theoretical value, and its Mn-content has been refined (Table 3). The $M(1)$ site, which is significantly larger than the $M(2)$ site, has been considered to be completely filled with Mn^{2+}. The refined occupancy factors of Mn^{2+} on $M(2)$ and $M(1)$ (Table 3) are in good agreement with the nominal compositions, and the $M(1)$–O and $M(2)$–O bond distances are similar in all these compounds (Table 4). In order to confirm the cationic distribution on the M sites, we calculated the bond valence sums for $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$, using the empirical parameters of *Brown* and *Altermatt* (1985). According to these authors, the bond valence, s, associated with the bond length, R, is given by the equation: $s = \exp[(R_0 - R)/0.37]$, where R_0 is 1.790 for Mn^{2+} and 1.759 for Fe^{3+}. Assuming that $M(1)$ is occupied by Mn^{2+}, and that $M(2)$ is occupied by Fe^{3+} and Mn^{2+}, we calculated bond valence sums of 1.87 for $M(1)$

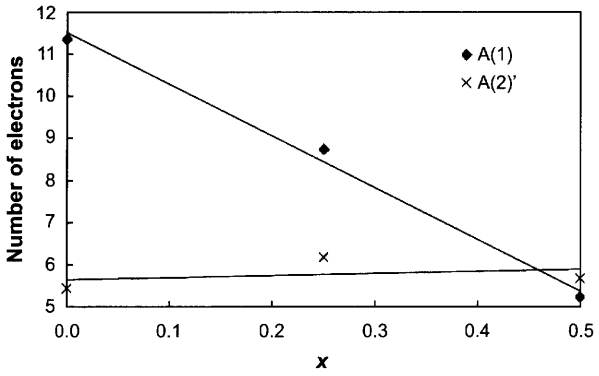

Fig. 3. Variation of the number of electrons on the A sites, for the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ alluaudite-type compounds. The error bars are smaller than the data points

and of 2.84 for $M(2)$. These bond valence sums are in fairly good agreement with the theoretical values of 2.00 and 2.75, respectively.

Whereas Na^+ occurs on both A sites for $x = 0.00$, the distribution of Na^+ and Li^+ between the $A(1)$ and $A(2)'$ crystallographic sites for $x = 0.25$ and 0.50 can be more accurately assessed than in the solid solutions investigated by *Hatert* et al. (2000, 2002). This is due to the number of vacancies per formula unit, which is only 0.5 for $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$, but 1.0 for $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$. Consequently, the electron densities occurring on the A sites in $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ are significantly higher than for the other solid solutions. This implies a more important variation of electronic density during the $Na^+ \rightarrow Li^+$ substitution. The variations of the number of electrons occurring on the A sites in $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$, calculated by adding the electrons according to the Na^+ and Li^+ site occupancy factors, are shown in Fig. 3. The fact that the number of electrons on the $A(1)$ site decreases, whereas the number of electrons on $A(2)'$ is approximately constant, indicates that the $Na^+ \rightarrow Li^+$ substitution probably takes place solely on the $A(1)$ site. This hypothesis is confirmed by the $A(1)$–O bond distances, which show a significant decrease with increasing x, when compared with the $A(2)'$–O bond distances (Table 4). The crystal structures of the compounds with $x = 0.25$ and $x = 0.50$ were finally refined assuming an occupation of $A(1)$ by Na^+ and Li^+, and of $A(2)'$ by Na^+ and vacancies. The Li-content of the $A(1)$ site was then fixed to its theoretical value, whereas the Na-content was refined. The resulting occupancy factors (Table 3) are in very good agreement with the nominal compositions, thus confirming the model used for the Rietveld refinements.

The a, b and c unit-cell parameters of the $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ alluaudite-type compounds (Table 1) show regular decreases, roughly linear, with increasing x (Fig. 4). These decreases result from the replacement of Na^+ by Li^+ on the $A(1)$ crystallographic site. It is important to note that the β angle increases linearly between $x = 0.00$ to 1.00, whereas the a, b and c unit-cell parameters are affected by a sudden change of slope occurring at $x = 0.70$ (Fig. 4). These changes of unit-cell parameters between 0.70 and 1.00 are not due to the incorporation of lithium into the channels of the alluaudite structure, but are probably related to the extraction of iron out of the structure, in order to form $Li_3Fe_2(PO_4)_3$. The decrease

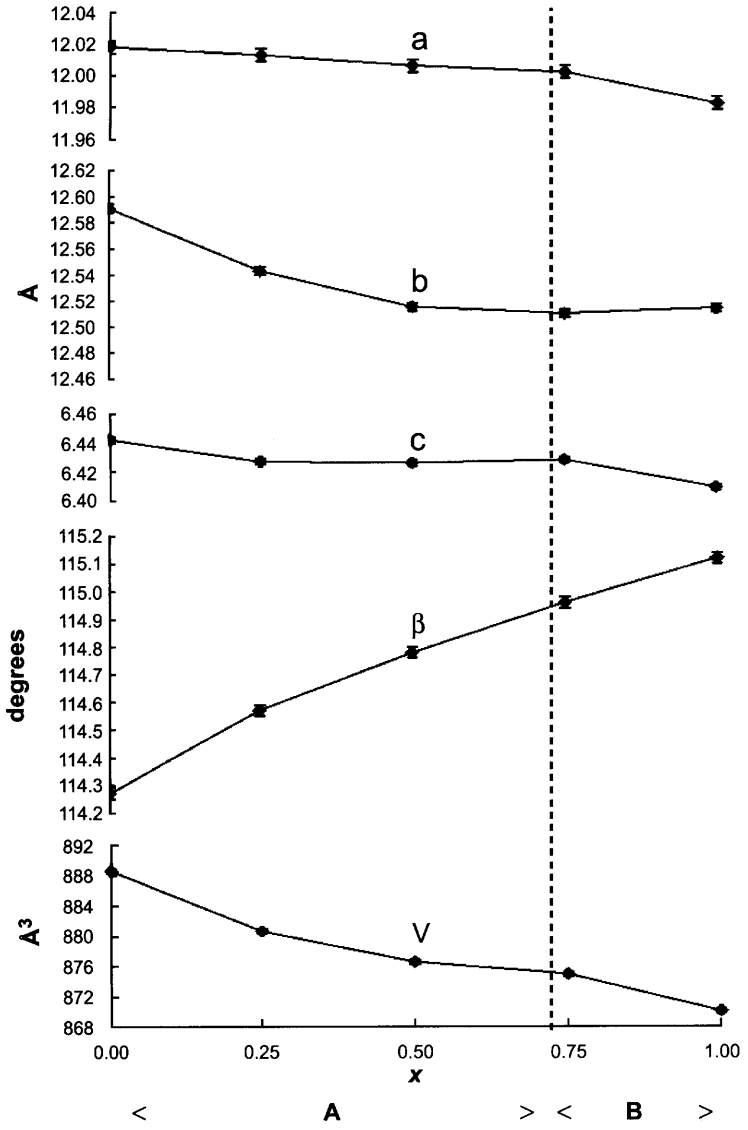

Fig. 4. Variation of the unit-cell parameters, for $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ alluaudite-type compounds. The error bars are smaller than the data points. **A** Pure alluaudite. **B** Alluaudite accompanied by $Li_3Fe_2(PO_4)_3$

of the unit-cell parameters between 0.00 and 0.70 (Fig. 4) correlate with the variations of bond distances induced by the incorporation of lithium into the alluaudite structure. The differences between the bond distances of $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ and $Na_{0.75}Li_{0.75}Mn_{1.5}Fe_{1.5}(PO_4)_3$, presented in Table 4, clearly indicate a significant decrease of the $A(1)$–O(2) and $A(1)$–O(4) bond distances. As already shown by *Hatert* et al. (2000, 2002), these bonds form a square parallel to the *b* axis, and for this reason, the decrease of the $A(1)$–O(2) and $A(1)$–O(4) bond distances provokes a more pronounced decrease of the *b* unit-cell parameter, when compared to the *a* and *c* parameters (Fig. 4).

Discussion and conclusions

The solid state synthesis of alluaudite-type compounds, in which Na^+ is progressively replaced by Li^+, permits to shed more light on the distribution of lithium in the alluaudite structure. As shown by *Hatert* et al. (2000, 2002) and in the present study, lithium is not localized on the small $M(2)$ site of the structure, as suggested by *Moore* (1971), but on the large $A(1)$ and/or $A(2)'$ crystallographic sites. The occurrence of lithium on large crystallographic sites is well known in the literature, and is favored by a partial occupancy (*Wenger* and *Armbruster*, 1991).

Whereas the unit-cell volumes of $NaMnFe_2(PO_4)_3$ and $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ are 877.3(2) and 888.6(2) $Å^3$, respectively, the unit-cell volume of $NaCdIn_2(PO_4)_3$ is 963.7(3) $Å^3$. This increase of ca. 10% of the unit-cell volume is induced by the replacement of Fe^{3+} and Mn^{2+} by In^{3+} and Cd^{2+}, respectively, on the M sites of the alluaudite structure. Consequently, the $A(1)$–O and $A(2)'$–O bond distances increase significantly, thus leading to a change of the coordination polyhedra morphologies of $A(1)$ and $A(2)'$ in $NaCdIn_2(PO_4)_3$. The distorted cube $A(1)$ and the gabled disphenoid $A(2)'$, observed in $NaMnFe_2(PO_4)_3$ and $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$, are better described in $NaCdIn_2(PO_4)_3$ as a distorted octahedron and a distorted trigonal prism, respectively. The distorted morphologies of $A(1)$ and $A(2)'$ resemble the morphology of the distorted cubic site of the garnet structure. This observation reflects the close relationship between the alluaudite and the garnet structures, already pointed out by *Moore* and *Molin-Case* (1974), and demonstrated by the existence of a garnet-alluaudite transition (*Khorari* et al., 1995, 1997, 1998).

Another consequence of the increase of the $A(1)$–O and $A(2)'$–O bond distances is the variation of the substitution limit x, which is much higher in $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ ($x = 0.90$) and $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ ($x = 0.70$) than in $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ ($x = 0.55$).

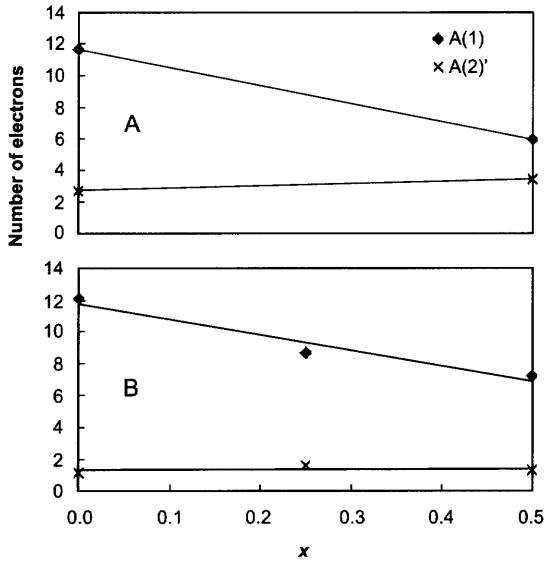

Fig. 5. Variation of the number of electrons on the A sites, for the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ (A) and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ (B) solid solutions. The error bars are smaller than the data points

Finally, the variations of the number of electrons occurring on the $A(1)$ and $A(2)'$ sites of $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ are shown in Fig. 5. This diagram is similar to that obtained for $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ (Fig. 3), with a decrease of the number of electrons on the $A(1)$ site, whereas the number of electrons on $A(2)'$ is approximately constant. This observation confirms that lithium is also localized on the $A(1)$ site in both the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ and $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$ alluaudite-type solid solutions.

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